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^{13}C NMR SPECTROSCOPY OF SOLANUM STEROID ALKALOIDS[1]

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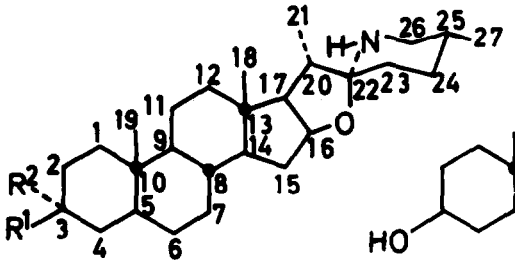
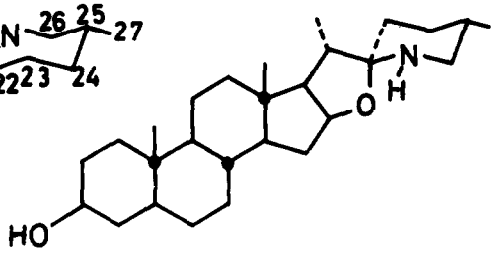
C_{27}-Steroidal alkaloids of the Solanum group are of great potential interest as starting materials in the synthesis of steroid hormone analogues, and new representatives are still being isolated from plants. Although very recently ^{13}C NMR spectroscopy was shown to be quite useful in the structure elucidation of two new 22,26-epimino-cholestanes, 25-isosolafloridine and solacallinidine[2], a systematic investigation of Solanum alkaloids has not yet been undertaken. Therefore we have measured the proton noise and off-resonance decoupled ^{13}C NMR spectra of the Solanum alkamines I - VIII of different structural types and assigned them as given in Table 1.

Saturated solutions in $CDCl_3$ were measured with a Bruker HX-90R spectrometer operating at 22.635 MHz (solvent deuterium provided a lock signal, proton noise decoupling at 90 MHz).

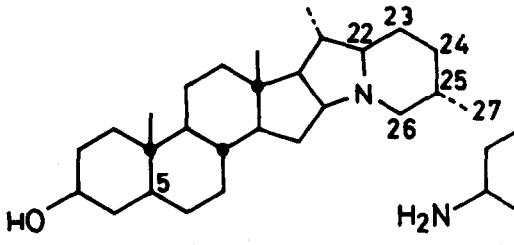
For the spirosolane alkaloids I - IV and jurubidine (VII) the assignment of the resonances was accomplished by comparison with the known data of steroid sapogenins[3] and androst-4-ene-3,17-dione[4] as well as by considering the shift differences δ(piperidine)[5] - δ(tetrahydropyran)[6] (considering ring F of the compounds I - IV) and δ(cyclohexylamine)[6] - δ(cyclohexanol)[5] (concerning ring A in VII). To aid the interpretation of the spectra of the solanidane alkaloids demissidine (V) and solanidine (VI), the chemical shifts of indolizidines[7] were considered. The carbon resonances of the piperidine ring of solanocapsine (VIII) were assigned by comparison with the data of the Veratrum alkaloid jervine[5], taking advantage of the reported substitu-



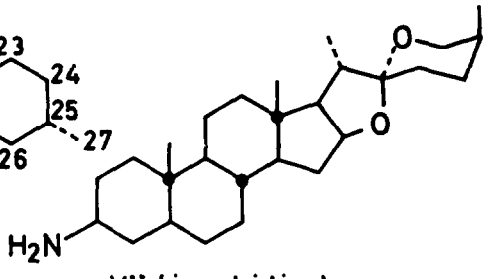
I: R^1 = OH, R^2 = H (soladulcidine)
II: R^1 = OH, R^2 = H, Δ^5 (solasodine)
III: $R^1 + R^2$ = O, Δ^4



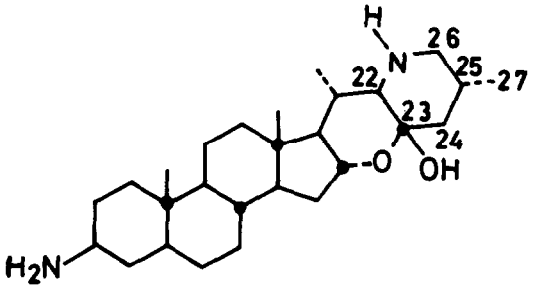
IV (tomatidine)



V (demissidine)
VI: Δ^5 (solanidine)



VII (jurubidine)



VIII (solanocapsine)

Tab. 1: ^{13}C Chemical Shifts of the Steroid Alkaloids I to VIII (in ppm relative to TMS)

C-atom	I	II	III	IV	V	VI	VII	VIII
1	37.0	37.3	35.7	37.0	37.1	37.3	37.7[+)]	37.6
2	31.5	31.5	33.9	31.5	31.6	31.6	30.9	30.1
3	71.1	71.7	199.2	71.0	71.3	71.7	50.9	51.2
4	38.2	42.3	123.8	38.2	38.3	42.3	37.6[+)]	39.3
5	44.9	140.9	170.9	44.9	45.0	140.8	45.5	45.8
6	28.6	121.3	32.8	28.6	28.8	121.6	28.6	28.7
7	32.3	32.1	32.1	32.3	32.3	32.1	32.3	32.5
8	35.2	31.5	35.2	35.0	35.4	31.6	35.2	35.1
9	54.4	50.2	53.8	54.4	54.6	50.2	54.5	55.1
10	35.6	36.7	38.6	35.5	35.6	36.7	35.6	35.7
11	21.1	20.9	20.8	21.1	21.1	21.0	21.0	20.5
12	40.1	40.0	39.8	40.2	40.2	40.0	40.1	39.3
13	41.0	40.5	40.6	40.9	40.6	40.3	40.6	41.9
14	56.3	56.6	55.6	55.8	57.4	57.6	56.4	55.1
15	32.1	32.1	32.1	32.6	33.5	33.3	31.7	33.1[+)]
16	80.0	79.0	78.5	78.5	69.0	69.1	80.9	74.5
17	62.6	62.9	62.7	62.0	63.3	62.9	62.1	60.6
18	16.5	16.4	16.5	16.9	17.1	16.8	16.5	13.7
19	12.4	19.3	17.4	12.3	12.4	19.4	12.3	12.3
20	41.6	41.3	41.2	43.0	36.7	36.7	42.2	46.3
21	15.0	15.2	15.2	15.8	18.3	18.1	14.3	15.1
22	98.3	98.4	98.2	99.3	74.7	74.7	109.7	68.9
23	33.3	34.1	34.1	26.6	29.3	29.1	27.1	96.1
24	29.6	30.3	30.3	28.6	31.1[+)]	30.9[+)]	25.8[++)]	39.3
25	30.3	31.5	31.3	31.0	31.3[+)]	31.1[+)]	26.0[++)]	31.9[+)]
26	46.9	47.7	47.6	50.2	60.2	60.2	65.1	55.1
27	19.1	19.3	19.3	19.3	19.5	19.4	16.1	18.7

+) ++) May be reversed.

ent effects of an axial hydroxyl group[8] (at C-23). The assignment of some signals of solanocapsine has to be regarded as tentative.

In comparison with the corresponding peak of soladulcidine (I), the C-23 signal of tomatidine (IV) is shifted upfield ($\Delta\delta$ = -6.7 ppm) because of γ-interaction with the methyl group C-21. The C-21 resonance has nearly the same position in both alkaloids because of γ-interaction with either CH_2 or NH. Interesting is the broad signal of C-22 in the spectrum of tomatidine (IV) pointing to a dynamic equilibrium, perhaps due to participation of a ring-E-open azomethine structure.[9]

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